Vapor−Liquid Equilibria of the Binary Systems Nitrogen + Bromotrifluoromethane, + Bromochlorodifluoromethane, + 1,1,1,2,3,3,3-Heptafluoropropane, and + Trifluoroiodomethane from 293.2 to 313.2 K and 30 to 100 bar

Jong Sung Lim* and Jae-Duck Kim

Division of Environmental and CFC Technology, Korea Institute of Science and Technology (KIST),
P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Isothermal vapor−liquid equilibria were measured in the binary systems nitrogen + bromotrifluoromethane, nitrogen + bromochlorodifluoromethane, nitrogen + 1,1,1,2,3,3,3-heptafluoropropane, and nitrogen + trifluoroiodomethane in a circulation-type equilibrium apparatus. The temperature range was (293.2 to 313.2) K and the pressure range was (30 to 100) bar. The experimental data were well correlated with the Peng−Robinson equation of state using the Wong and Sandler mixing rule, and the relevant parameters are presented.

Introduction

Bromotrifluoromethane (halon-1301) and bromochlorodifluoromethane (halon-1211) have been used as clean, nontoxic, and effective fire extinguishing agents for a long time. But these compounds are being phased out because of their ozone-depletion potential. 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) and trifluoroiodomethane (CF_3I) are known to be promising replacement agents of halon-1301 and halon-1211.

The vapor−liquid equilibrium data for the systems nitrogen + clean fire extinguishing agents are essential because nitrogen is used as a pressurization gas to shorten the discharging time of the agents. This information is important because it will provide safety guidelines for the pressure vessels. The amount of nitrogen needed to pressurize the vessel plays a major role in the determination of the final pressure of the vessel because if the amount of pressurization gas is significant, a dangerously high pressure may result when the vessel is exposed to elevated temperatures (Yang et al., 1993). Very few experimental data (Yang et al., 1993, 1995), however, have been previously reported in the literature.

In this work, we measured the vapor−liquid equilibria for the binary systems nitrogen + halon-1301, nitrogen + halon-1211, nitrogen + HFC-227ea, and nitrogen + CF_3I in the temperature range (293.2 to 313.2) K and pressure range (30 to 100) bar. The experimental data were correlated with the Peng−Robinson equation of state (1976) using the Wong and Sandler mixing rule (1992).

Experimental Section

Chemicals. The purities of the chemicals used in this work were guaranteed by the manufacturers as shown in Table 1. They were used without any further purification.

Experimental Apparatus. The experimental approach for the phase equilibrium measurements in the present work adopted a circulation type apparatus in which both vapor and liquid phases were continuously recirculated. The experimental apparatus used in this work is the same as used in the previous work (Lim et al. 1994, 1996). The system consists of five major parts: an equilibrium cell, duplex circulation pump, hand pump, vapor and liquid sampling valves, and a temperature-controlled air bath. The temperatures in the cell were measured by a K-type thermocouple (OMEGA Co.), and a digital indicator (OMEGA model DP41-TC) which was calibrated by KRISS (Korea Institute of Standards and Science) with an uncertainty of ±0.1 K. The pressure in the cell was measured by a Heise pressure gauge (Model CMM 104637) which was calibrated by a dead weight gauge (NAGANO KEIKI PD12) with a measuring accuracy of ±0.01 bar. The hand pump (HIP model 62-6-10) was equipped to manually adjust the system pressure to the desired pressure within ±0.01 bar.

Table 1. Suppliers and Purities of the Chemicals Used

component	supplier	purity/ mass %
nitrogen	Shin-Yang Chemical Co., Seoul, Korea	>99.9
bromotrifluoromethane (halon-1301)	Hanju Chemical Co., Hwasung, Korea	>99.9
bromochlorodifluoromethane (halon-1211)	Hanju Chemical Co., Hwasung, Korea	>99.5
1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea)	Great Lakes Chemical Co., West Lafayette, IN	>99.9
trifluoroiodomethane (CF_3I)	Pacific Sci. Co., Duarte, CA	>99.9

Experimental Procedure. Each experiment was started by evacuating the apparatus. A certain amount of halon or halon replacement agent was supplied to the equilibrium cell. By controlling the temperature of the air bath, the temperature of the entire system was maintained constant. After the desired temperature was attained, a proper amount of nitrogen was introduced into the cell from a charging cylinder until the system pressure was to be around the desired pressure. Both vapor and liquid phases were allowed to circulate for about 1 h to ensure equilibrium. During circulation, the system pressure was adjusted minutely to the desired equilibrium pressure using the hand pump. After equilibrium was attained, vapor and liquid samples were then taken from the recycling lines by use of the vapor sampling valve with the loop volume of 5 μL and the liquid sampling valve with the loop volume of 1 μL. They were directly injected into the gas chromatograph (HP-5890 series II) equipped with TCD and column packed with Porapak Q (Alltech Co.) which is connected on-line to both vapor and liquid sampling valves.

We measured the equilibrium concentration at least three times to obtain reliable values. Average deviations

---

* To whom correspondence should be addressed. E-mail: limjs@kistmail.kist.re.kr.

S0021-9568(96)00239-7 CCC: $14.00

Table 2. Vapor−Liquid Equilibrium Measurements for the Nitrogen (1) + Halon-1301 (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
T/K = 293.2					
0.0813	0.5048	40.00	0.2150	0.6049	80.00
0.1108	0.5542	50.00	0.2578	0.5977	90.00
0.1430	0.5852	60.00	0.3105	0.5771	100.00
0.1762	0.6022	70.00			
T/K = 303.2					
0.0692	0.3944	40.00	0.2176	0.5051	80.00
0.1044	0.4587	50.00	0.2753	0.4692	90.00
0.1384	0.4903	60.00	0.2811	0.4613	91.00
0.1741	0.5073	70.00	0.2859	0.4482	92.00
T/K = 313.2					
0.0589	0.2811	40.00	0.1768	0.3931	70.00
0.0927	0.3478	50.00	0.2003	0.3854	74.00
0.1299	0.3853	60.00	0.2167	0.3627	77.00

Table 3. Vapor−Liquid Equilibrium Measurements for the Nitrogen (1) + Halon-1211 (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
T/K = 293.2					
0.0447	0.8822	30.00	0.1019	0.9331	70.00
0.0598	0.9091	40.00	0.1193	0.9350	80.00
0.0742	0.9196	50.00	0.1346	0.9365	90.00
0.0894	0.9282	60.00	0.1466	0.9369	100.00
T/K = 303.2					
0.0456	0.8596	30.00	0.1050	0.9145	70.00
0.0607	0.8854	40.00	0.1212	0.9160	80.00
0.0772	0.8986	50.00	0.1378	0.9179	90.00
0.0907	0.9086	60.00	0.1532	0.9190	100.00
T/K = 313.2					
0.0448	0.8120	30.00	0.1059	0.8822	70.00
0.0616	0.8442	40.00	0.1205	0.8885	80.00
0.0756	0.8684	50.00	0.1378	0.8889	90.00
0.0896	0.8794	60.00	0.1535	0.8986	100.00

Table 4. Vapor−Liquid Equilibrium Measurements for the Nitrogen (1) + HFC-227ea (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
T/K = 293.2					
0.0946	0.7941	30.00	0.2146	0.8588	70.00
0.1219	0.8253	40.00	0.2451	0.8622	80.00
0.1549	0.8426	50.00	0.2752	0.8623	90.00
0.1876	0.8542	60.00	0.3072	0.8624	100.00
T/K = 303.2					
0.0880	0.7344	30.00	0.2165	0.8205	70.00
0.1229	0.7705	40.00	0.2492	0.8213	80.00
0.1553	0.7958	50.00	0.2808	0.8221	90.00
0.1882	0.8128	60.00	0.3149	0.8186	100.00
T/K = 313.2					
0.0836	0.6565	30.00	0.2151	0.7715	70.00
0.1173	0.7103	40.00	0.2479	0.7718	80.00
0.1497	0.7412	50.00	0.2857	0.7727	90.00
0.1812	0.7583	60.00	0.3019	0.7696	100.00

of the equilibrium concentration were ±0.001 (mole fraction) for both liquid and vapor phases.

Results and Discussion

The experimental data for isothermal vapor−liquid equilibria (VLE) for the binary systems of nitrogen (1) + halon-1301 (2), nitrogen (1) + halon-1211 (2), nitrogen (1) + HFC-227ea (2), and nitrogen (1) + CF_3I (2) are shown in Tables 2−5, respectively. Each table lists the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium. Experiments for all systems except nitrogen + halon-1301 were performed in the temperature range (293.2 to 313.2) K and pressure range (30 to 100) bar. For the nitrogen + halon-1301 system, experiments were performed below 92 bar at 303.2 K and 77 bar at 313.2 K, due to the critical points of the system.

Table 5. Vapor−Liquid Equilibrium Measurements for the Nitrogen (1) + CF_3I (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
T/K = 293.2					
0.0608	0.7922	30.00	0.1437	0.8684	70.00
0.0811	0.8282	40.00	0.1660	0.8726	80.00
0.1022	0.8487	50.00	0.1845	0.8768	90.00
0.1255	0.8628	60.00	0.2075	0.8774	100.00
T/K = 303.2					
0.0588	0.7359	30.00	0.1470	0.8365	70.00
0.0798	0.7850	40.00	0.1680	0.8415	80.00
0.1029	0.8063	50.00	0.1895	0.8465	90.00
0.1243	0.8267	60.00	0.2102	0.8493	100.00
T/K = 313.2					
0.0572	0.6764	30.00	0.1469	0.7936	70.00
0.0796	0.7270	40.00	0.1688	0.7991	80.00
0.1020	0.7605	50.00	0.1950	0.8027	90.00
0.1262	0.7802	60.00	0.2153	0.8063	100.00

Table 6. Characteristic Properties of the Chemicals

component	T_c/K	P_c/bar	ω	data source
nitrogen	126.26	34.0	0.039	Braker et al. (1976)
halon-1301	340.15	39.7	0.171	TRC Tables (1996)
halon-1211	426.9	42.6	0.184	TRC Tables (1996)
HFC-227ea	374.8	29.1	0.357	Robin (1994)
CF_3I	395.0	40.4	0.273	Nimitz (1994)

Table 7. Values of Binary Parameters and AAD (%) of *P* and *y*

system	NRTL params[a]	AAD[b]/%		
		293.2 K	303.2 K	313.2 K
N_2 + halon-1301	$k_{ij} = 0.5460$ $A_{ji} = 0.9854$ $A_{ij} = 0.2996$	0.96	1.19	2.92
N_2 + halon-1211	$k_{ij} = 0.6922$ $A_{ji} = -1.3622$ $A_{ij} = 4.6525$	0.85	2.44	1.94
N_2 + HFC-227ea	$k_{ij} = 0.5792$ $A_{ji} = -2.7547$ $A_{ij} = 8.6937$	1.26	0.57	2.70
N_2 + CF_3I	$k_{ij} = 0.4589$ $A_{ji} = -1.6167$ $A_{ij} = 12.8562$	0.91	1.75	3.29

[a] Binary parameters for all systems were obtained at 293.2 K and the unit of A_{ij} and A_{ji} is kJ/mol. [b] AAD = $(1/N)\Sigma_i^N|(P_{\mathrm{exptl},i} - P_{\mathrm{calcd},i})/P_{\mathrm{exptl},i}| \times 100$.

The VLE data were correlated with the Peng−Robinson equation of state (Peng and Robinson, 1976). The Peng−Robinson equation of state is expressed as follows:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{1}$$

$$a = (0.457235R^2T_c^{\ 2}/P_c)\alpha(T) \tag{2}$$

$$b = 0.077796RT_c/P_c \tag{3}$$

$$\alpha(T) = [1 + \kappa(1 - T_r^{\ 0.5})]^2 \tag{4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where the parameter a is a function of temperature, b is constant, κ is a constant characteristic of each substance, ω is the acentric factor, P is pressure, P_c is the critical pressure, T is absolute temperature, T_c is the critical temperature, T_r is the reduced temperature, and v is molar volume.

In this work, we used the Wong−Sandler mixing rule (Wong and Sandler, 1992) to obtain equation of state

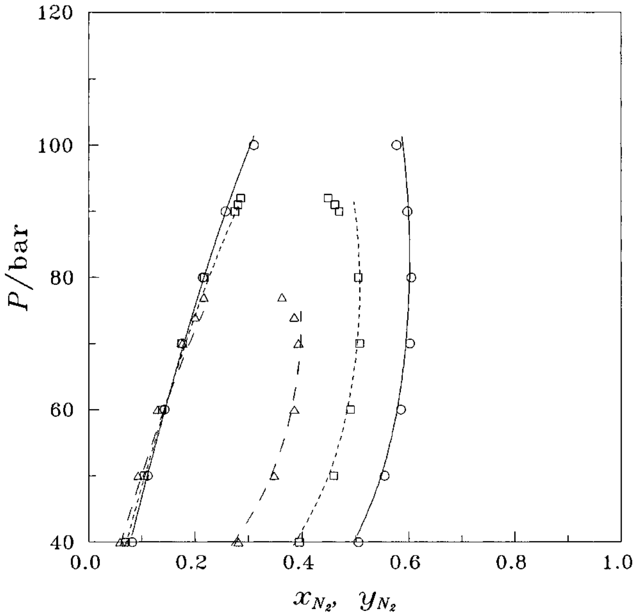

Figure 1. $P-x-y$ diagram for the nitrogen (1) + halon-1301 (2) system at 293.2 K, 303.2 K, and 323.2 K: (○) experimental at 293.2 K; (□) experimental at 303.2 K; (△) experimental at 313.2 K; (—) calculated at 293.2 K; (- - -) calculated at 303.2 K; (— — —) calculated at 313.2 K.

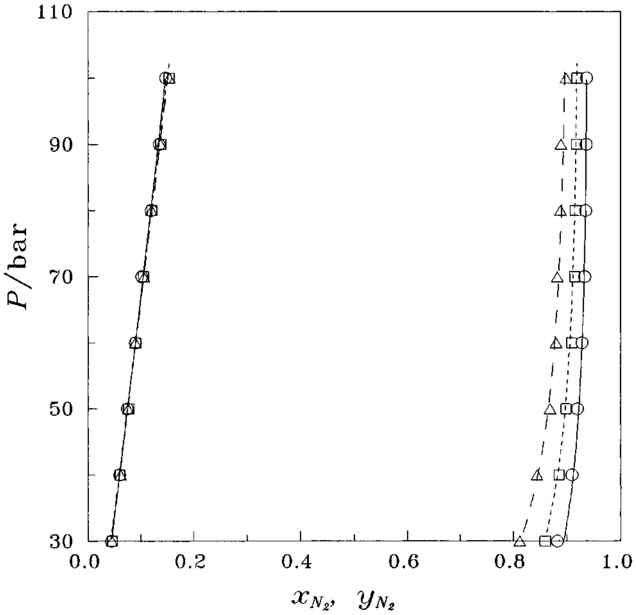

Figure 2. $P-x-y$ diagram for the nitrogen (1) + halon-1211 (2) system at 293.2 K, 303.2 K, and 323.2 K: (○) experimental at 293.2 K; (□) experimental at 303.2 K; (△) experimental at 313.2 K; (—) calculated at 293.2 K; (- - -) calculated at 303.2 K; (— — —) calculated at 313.2 K.

parameters for a mixture from those of the pure components. This mixing rule for a cubic equation of state can be written as

$$b_{\mathrm{m}} = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{(1 - A^{\mathrm{E}}_{\infty}/CRT - \sum_i x_i a_i/RTb_i)} \qquad (6)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2}[(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \qquad (7)$$

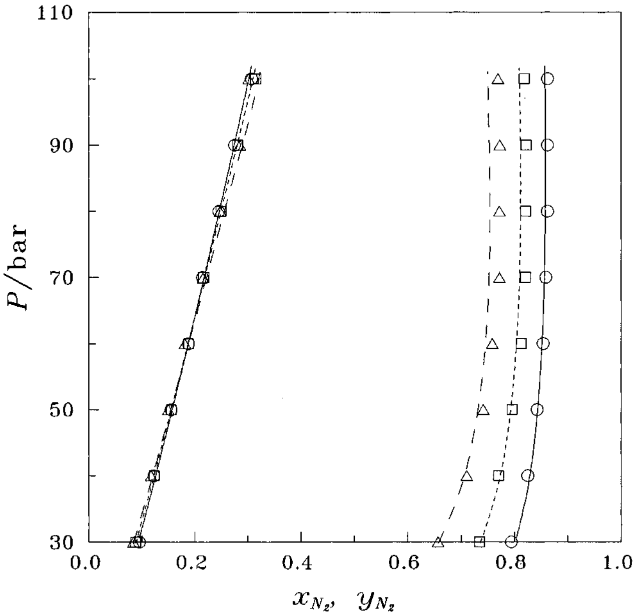

Figure 3. $P-x-y$ diagram for the nitrogen (1) + HFC-227ea (2) system at 293.2 K, 303.2 K, and 323.2 K: (○) experimental at 293.2 K; (□) experimental at 303.2 K; (△) experimental at 313.2 K; (—) calculated at 293.2 K; (- - -) calculated at 303.2 K; (— — —) calculated at 313.2 K.

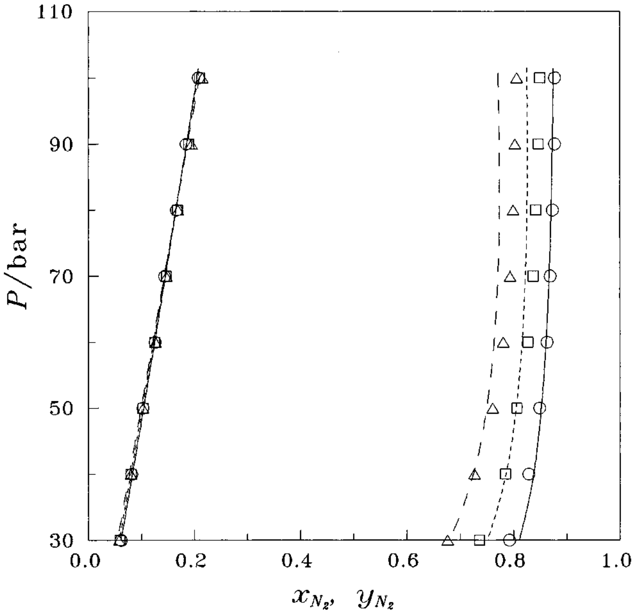

Figure 4. $P-x-y$ diagram for the nitrogen (1) + HFC-CF$_3$I (2) system at 293.2 K, 303.2 K, and 323.2 K: (○) experimental at 293.2 K; (□) experimental at 303.2 K; (△) experimental at 313.2 K; (—) calculated at 293.2 K; (- - -) calculated at 303.2 K; (— — —) calculated at 313.2 K.

and

$$\frac{a_{\mathrm{m}}}{b_{\mathrm{m}}} = \sum_i x_i \frac{a_i}{b_i} + \frac{A^{\mathrm{E}}_{\infty}}{C} \qquad (8)$$

where C is a numerical constant equal to ln($2^{1/2} - 1/2^{1/2}$ for the Peng−Robinson equation (1976) used in this work. Also, A^{E}_{∞} is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy model (Wong *et al.*, 1992); in this study we use the NRTL model (Renon and Prausnitz, 1968):

$$\frac{A_\infty^{\mathrm{E}}}{RT} = \sum_i x_i \frac{(\sum_j x_j G_{ji}\tau_{ji})}{\sum_k x_k G_{ki}} \qquad (9)$$

with

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \qquad \text{and} \qquad \tau_{ij} = A_{ji}/(RT) \qquad (10)$$

where G_{ij} is the local composition factor for the NRTL model, τ_{ij} is the NRTL model binary interaction parameter, $A_{ij} = (g_{ij} - g_{jj})$ and g_{jj} is an interaction energy parameter of $i-j$, α_{ij} is the nonrandomness parameter, and R is the gas constant (8.314 J/(K mol)).

The critical properties (T_c, P_c) and acentric factors (ω) of nitrogen, halon-1301, halon-1211, HFC-227ea, and CF_3I used to calculate the parameters for the Peng−Robinson equation of state are given in Table 6. We have set the nonrandomness parameter, α_{ij}, equal to 0.3 for all the binary mixtures studied here.

The Marquardt algorithm (Kuester and Mize, 1973) was applied to obtain the parameters with the following objective function:

$$\mathrm{obj} = \sum_j \left(\frac{P_{j,\mathrm{exptl}} - P_{j,\mathrm{calcd}}}{P_{j,\mathrm{exptl}}}\right)^2 + \sum_j (y_{j,\mathrm{exptl}} - y_{j,\mathrm{calcd}})^2 \qquad (11)$$

In these calculations the VLE at 303.2 K and 313.2 K were predicted using the model parameters obtained at 293.2 K. Because the temperature ranges of binary systems studied here were relatively short, k_{ij}, A_{ij}, and A_{ji} were fixed with the values obtained at 293.2 K. All the binary parameters of both systems and the average absolute deviations (AAD) between measured and calculated values are listed in Table 7.

Figures 1−4 show the comparison of measured and calculated values for nitrogen (1) + halon-1301 (2), nitrogen (1) + halon-1211 (2), nitrogen (1) + HFC-227ea (2), and nitrogen (1) + CF_3I (2) from 293.2 K to 323.2 K, respectively. As shown in these figures and by the low AAD, the calculated values give a good agreement with the experimental data. From these results, the NRTL binary parameters obtained in this work can be used for the prediction of VLE in the range of temperatures studied. For the nitrogen (1) + halon-1301 (2) system, the following critical pressures were observed; about 108 bar at 293.2 K, 96 bar at 303.2 K, and 81 bar at 313.2 K, respectively. Other systems exhibited no critical point at these experimental conditions.

Literature Cited

Braker, W.; Mossman, A. L. *The Matheson Unabridged Gas Data Book*; Matheson: East Rutherford, NJ, 1976.

Kuester, J. L.; Mize, J. H.; *Optimization Techniques with Fortran*; McGraw-Hill: New York, 1973.

Lim, J. S.; Lee, Y. Y.; Chun, H. S. Phase Equilibria for Carbon Dioxide-Ethanol-Water System at Elevated Pressures. *J. Supercrit. Fluids* **1994**, *7*, 219−230.

Lim, J. S.; Lee, Y. W.; Kim, J. D.; Lee, Y. Y.; Lee, J. C. Vapor-Liquid Equilibria for 1,1-Difluoroethane + Acetylene, and 1,1-Difluoroethane + 1,1-Dichloroethane at 303.2 and 323.2 K. *J. Chem. Eng. Data* **1996**, *41*, 1168−1170.

Nimitz, J. Trifluoromethyl Iodide and its Blends as High-Performance, Environmentally Sound Halon 1301 Replacements. Proceedings of Halon Options Technical Working Conference, May 3−5, 1994, Albuquerque, NM.

Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 5−144.

Robin, M. L. Thermophysical Properties of HFC-227ea. Proceedings of '94 International CFC Halon Alternatives Conference, Oct 24, 1994, Washington, DC.

TRC Databases for Chemistry and Engineering - TRC Thermodynamic Tables Version 1996-1S. Texas A&M University System: College Station, TX, 1996.

Wong, D. S. H.; Sandler, S. I. A Theoretically Correct Mixing Rule for Cubic Equation of State. *AIChE J.* **1992**, *38*, No. 5, 671−680.

Wong, D. S. H.; Orbey, H.; Sandler, S. I. An equation of state mixing rule for nonideal mixtures using available activity coefficient model parameters and which allows extrapolation over large ranges of temperature and pressure. *Ind. Eng. Chem. Res.* **1992**, *31*, 2033−2039.

Yang, J. C.; Breuel, B. D.; Grosshandler, W. L. Solubilities of Nitrogen and Freon-23 in Alternatives Halon Replacement Agents. Proceedings of Halon Alternatives Technical Working Conference, May 11−13, 1993, Albuquerque, NM.

Yang, J. C.; Huber, M. L.; Boyer, C. I. A Model for Calculating Alternative Agent/Nitrogen Thermodynamics Properties. Proceedings of Halon Options Technical Working Conference, May 9−11, 1995, Albuquerque, NM.

Received for review July 12, 1996. Accepted October 9, 1996.⊗

JE960239O

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1996.